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(54) Isopropyl t-butyl ether generation from crude acetone.

(57) Disclosed is a two-step process for the generation of isopropyl t-butyl ether from a crude by-product acetone stream which comprises :

a) Hydrogenating said crude acetone over a bulk metal, nickel-rich catalyst to give an isopropanol-rich effluent ;

b) subjecting said isopropanol-rich intermediate to etherification conditions in the presence of a strong acid catalyst selected from :

- (1) a cationic resin ;
- (2) a β-zeolite ;
- (3) dealuminised Y-zeolites ; and
- (4) metal-modified β-zeolites.

The process may also be used for the co-generation of isopropyl t-butyl ether and methyl t-butyl ether where the crude acetone stream additionally contains significant quantities of both methanol and t-butanol.

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This invention concerns a novel two-step procedure for generation of isopropyl *t*-butyl ether (IPTBE), and optionally methyl *t*-butyl ether (MTBE), from a crude by-product acetone stream which comprises (1) hydrogenating the crude acetone stream over a bulk-metal nickel-rich catalyst to give an isopropanol-rich effluent; and (2) subjecting the isopropanol-rich intermediate to etherification conditions in the presence of a series of strong acid catalysts selected from the group consisting of cationic resins, β -zeolites, metal-modified β -zeolites and dealuminised Y-zeolites.

IPTBE is useful as an octane enhancer in gasoline.

It is known to those skilled in the art that ethers, including both symmetrical and asymmetrical ethers, may be prepared by reacting an alcohol with another alcohol to form the desired product. The reaction mixture, containing catalyst and/or condensing agent may be separated and further treated to permit attainment of the desired product. Such further treatment commonly includes one or more distillation operations.

Though MTBE is the most widely produced and discussed ether as an automotive fuel additive, other ethers are also being evaluated, such as diisopropyl (DIPE) and ethyl tertiary butyl ether (ETBE). DIPE can be produced from refinery propylene and water and isopropanol is an intermediate in this process. In a variation, isopropyl tertiary butyl ether could be produced by combining isobutylene with isopropanol.

The higher molecular weight ethers all have blending vapor pressures lower than MTBE, and much lower than ethanol. Their boiling temperatures are also higher than MTBE. Furthermore, higher molecular weight IPTBE and ETBE have the potential to contribute more octane. IPTBE has the capability of providing the greatest net octane increase, (R+M)/2, of all the oxygenates considered as fuel additives to gasoline. In addition, because of their lower oxygen content, a greater volume of the higher MW ethers, such as IPTBE, can be added to base gasoline without exceeding the target oxygen content.

Although there has not been as much discussion regarding the production of IPTBE as there has been for MTBE, it is apparent that with its lower oxygen level and lower vapor pressure, there should be a definite niche for IPTBE in the future of reformulated gasoline.

With regard to classes of solid acid catalysts found suitable in this invention for IPTBE synthesis one of the earliest disclosures of zeolite beta was in U.S. Patent No. 3,308,069 (1967) to Wadinger et al.

In U.S. Patent No. 3,955,939, to Sommer et al. (1976), there is disclosed the production of a water-free mixture of isopropyl alcohol, diisopropyl alcohol, diisopropyl ether and by-products by the catalytic hydration of propylene in the gaseous phase at temperatures of 140°-170°C, wherein the water-free mixture formed according to the process can be used directly as an additive to gasoline fuel.

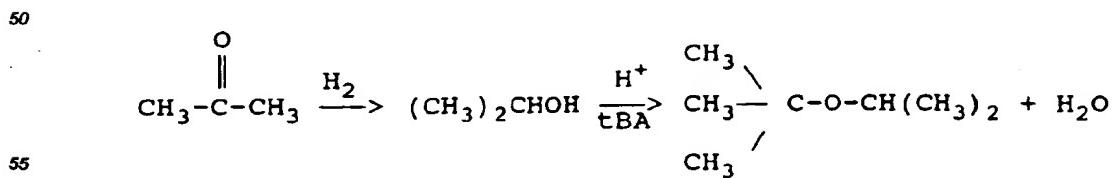
None of the available references would seem to suggest the conversion of the acetone portion present in a by-product stream into IPTBE. The portion of said by-product stream which typically comprises acetone is about 10% to 80%. It would greatly enhance the economics of any process to produce oxygenates if acetone from a by-product stream could be converted to useful oxygenate products such as isopropyl tertiary butyl ether, as well as methyl tertiary butyl ether (MTBE).

In accordance with the foregoing the novel method of the present invention for generation of isopropyl tertiary butyl ether from a crude by-product acetone stream is a two-step process which comprises:

- (1) hydrogenating the crude acetone stream over a bulk-metal nickel-rich catalyst to give an isopropanol rich effluent; and
- (2) Etherifying the isopropanol-rich intermediate in the presence of a series of strong acid zeolite catalysts selected from the group consisting of cationic resins, β -zeolite, metal-modified β -zeolites and dealuminised Y-zeolites.

Cogeneration of isopropyl tertiary butyl ether along with methyl *t*-butyl ether may also be accomplished in the present invention by the steps listed above, where the crude acetone stream, in addition, contains significant quantities that is preferably greater than 5% of both methanol (MeOH) and *t*-butanol (tBA). Most preferably, for the cogeneration of IPTBE and MTBE, the crude acetone feed contains 10%-40% each of both methanol and *t*-butanol.

The two-step IPTBE synthesis can be represented by:



(Eq. 1)

In a process to make propyl ne-xide a large number of by-products are typically generated with the desired product. These by-products may include formic acid, acetic acid, their ester derivatives, *t*-butanol and acetone. The acetone may constitute about 10% to 80% of certain crude by-product streams. These crude acetone streams may be further mixed with methanol.

5 In the first step of the present invention the crude acetone is passed over a nickel-rich catalyst. A preferred nickel catalyst is characterized by having the composition, calculated in mol%, of from about 60%-85% nickel, 1%-30% copper and 0.1%-6% chromium with the preferred proportions being about 65%-78% nickel, 10%-20% copper and 1%-3% chromium. The temperature necessary to achieve the desired acetone hydrogenation to isopropanol (IPA) is >100°C, the preferable range is 120°-180°C.

10 The conversion of acetone to isopropanol in the first step of Eq. 1 is normally >90% per pass in continuous processing and preferably it is as great as 99% or more. In the second step the isopropanol is subjected to etherification conditions in the presence of a series of solid strong acid catalysts, from the group consisting of cationic resins, (β -zeolite, metal-modified β -zeolites and a dealuminised Y-zeolite.

15 The ion exchange resins used as catalysts comprise a class of ion exchange resins having a strongly acidic cation exchange. These include the gel type, or macroreticular ion exchange resin, with sulfonic acid ($-\text{SO}_3\text{H}$), or substituted sulfonic acid functional groups, wherein the sulfonic acid functional group is bonded directly or indirectly to an organic, preferably polystyrene or styrene-divinylbenzene polymer backbone. Examples of such resins include AMBERLYST®-15 and XN-1010, AMBERLITE® IR-118, DOWEX® 50X2-100 and 5X8-100, DOWEX® M-31 and M-32, plus BIO RAD® AG50W-X2 and AMBERSEPTM 252H. Another suitable ion exchange resin is Rohm and Haas' A-35 high temperature resin, as well as DuPont's NAFION® resin, having the perfluorosulfonic acid functionality. Preferred are the macroporous resins with the styrene-divinylbenzene polymer backbone, sulfonic acid functionality, and 1%-20% cross-linking, such as AMBERLYST® 15 and XN-1010. Said resins should be in the acid (hydrogen) form.

20 The second group of exemplified catalysts includes β -zeolite, alone or modified. Typically, β -Zeolit is a crystalline aluminosilicate having a pore size greater than 5 Angstroms. The composition of the zeolite in its synthesized form may be expressed as follows:



25 where X is less than 1, preferably less than 0.7; TEA represents the tetraethylammonium ion; Y is greater than 5 but less than 100; and W is up to about 60 (it has been found that the degree of hydration may be higher than originally determined, where W was defined as being up to 4), depending on the degree of hydration and the metal cation present. The TEA component is calculated by differences from the analyzed value of sodium and the theoretical cation to structural aluminum ratio of unity.

30 It has been reported that zeolite beta has two types of three dimensional pore openings, the linear and the tortuous channel. The former has pore openings of $7.5\text{\AA} \times 5.7\text{\AA}$ and the latter has pore openings of $6.5\text{\AA} \times 5.6\text{\AA}$. When silica, for example, is deposited on zeolite beta, the pore opening was narrowed or blocked by the deposited silica. It was concluded that silica deposition selectively removes strong acid sites and increases the population of medium acid sites.

35 In the fully base-exchanged form, zeolite beta has the composition:



40 where X, Y and W have the values listed above and n is the valence of the metal M. This form of the zeolite may be converted partly to the hydrogen form by calcination, e.g. at 200°C to 900°C or higher. The completely hydrogen form may be made by ammonium exchange followed by calcination in air or an inert atmosphere such as nitrogen.

45 The preferred forms of zeolite beta are the highly acidic, high silica forms, having silica-to-alumina mole ratio of at least 10:1, and preferably in the range of 10:1 to 50:1 in the as-synthesized form, and a surface area of at least 100 m²/g.

50 Suitable β -zeolites for the practice of this Invention include Valfor C806 β , Valfor CP815 β and Valfor C861. Valfor® is the registered trademark of the PQ Corporation.

55 Valfor® C806 β zeolite is zeolite beta powder in template cation form. It is a high silica shape selective zeolite which contains the organic template used in the crystallization step, having been isolated after filtration and washing of the synthesis product. C806 β has a SiO₂/Al₂O₃ molar ratio of 23-26; the crystal size is 0.1-0.7 um; the surface area after calcination is about 700-750 m²/g; the cyclohexane adsorption capacity after calcination is 19-24g/100g; Na₂O content is about 0.01-1.0% by weight anhydrous; and, the organic content is about 11-13% by weight, on a water-free basis.

55 Valfor® C815 β zeolite is a calcined zeolite beta powder in hydrogen, sodium form. It is similar to C806 β except the product has been calcined to decompose the organic template. C815 β is a high silica, shape selective aluminosilicate with a large pore diameter. C815 β also has a SiO₂/Al₂O₃ molar ratio of about 23-26; the crystal size, surface area, cyclohexane adsorption capacity and Na₂O are all within the same ranges as given

for C806 β ,

Valfor® C861 β is an extrudate made of 80% C815 β powder and 20% alumina powder.

Said β -zeolites may optionally be pretreated before modification with a halogen, a halogen-containing organic compound, or a halogen-containing acid. Said halogen may be fluorine, chlorine, bromine or iodine, but is preferably fluorine. In the case of fluoride treatment, the fluoride content of the treated β -zeolite may be in the range of 0.1 to 10 wt%, but preferably is about 1%. Said fluoride-treated zeolites may optionally be calcined, at temperatures of 200°C and above, prior to further usage or modification.

Said catalysts may be formed in the presence of a binder, such as Group III or Group IV oxide. Group IV oxides used in conjunction with said β -zeolite include oxides of aluminum, silicon, titanium, zirconium, hafnium, germanium, tin and lead, as well as combinations thereof. Alumina is preferred. Said binders may comprise 10% to 90% of the formed catalyst.

Particularly effective in the subject cogeneration of IPTBE and MTBE are the β -zeolites modified with multiple metals. The metals useful for modifying the zeolite in the present invention comprise those from Groups IB, VB, VIB, VIIB and VIII of the Periodic Table, including said transition metals. Preferred metals are those found in Groups IB, VIB, VIIB and VIII of the Periodic Table and include copper, chromium, manganese, iron, nickel, palladium and platinum. Especially good results were observed using combinations of iron, manganese and chromium, or combinations of nickel and copper on Valfor® Zeolite 861 β , as well as platinum, or palladium, fluoride-modified β -zeolites.

Said zeolites are preferably impregnated with said specified metals as their salts, particularly their metal nitrate or chloride salts, in an aqueous, alcoholic, or ketonic media over a period of 1-24 hours, then the solids are filtered off, dried at elevated temperature, e.g. 120°C, for a period of time and calcined at 300-800°C for a further period, e.g. 315°C for 2 hours, followed by 540°C for another 2 hours, then reduced in a stream of hydrogen at $\geq 200^\circ\text{C}$.

The amount of the various metals deposited on the zeolite can vary. The amount of each individual metal, i.e., iron, chromium, copper, manganese, and nickel, can vary from 0.01 to 10.0%. Where iron, chromium and manganese are deposited on 861 β the preferred weight percent is from 0.1% to 5.0%.

The fourth type of catalyst suitable for the second stage of this invention generally comprises dealuminised Y-zeolite catalysts.

The preferred catalysts for use in the dealuminised form for the reaction of Eq. 1 are certain crystalline aluminosilicate zeolites, particularly the isostructural group of faujasite zeolites that include the synthetic X- and Y-zeolites. The preferred zeolites for dealumination are the Y-zeolites.

The unit cells of faujasite zeolites are cubic, $a_0 \approx 2.5$ nm, and each contains 192 silicon- or aluminium-centered oxygen tetrahedra which are linked through shared oxygen atoms. Because of the net negative charge on each of the aluminium-centered tetrahedra, each unit cell contains an equivalent number of charge-balancing cations. These are exclusively sodium ions in zeolites in their synthesized form. Typical cell contents for the Y-zeolites in the hydrated form are:



Y-zeolites are distinguished on the basis of the relative concentration of silicon and aluminum atoms and the consequent effects on detailed structure and related chemical and physical properties. The aluminum atoms in the unit cell of Y-zeolite vary from 76 to 48, resulting in a Si:Al ratio between 1.5 and 3.0. Both the cation concentration and charge density on the aluminosilicate structure are lower for Y-zeolites than for X-zeolites, where the aluminum atoms in the unit cell vary from 96 to 77.

The feature which determines the difference between faujasites and other zeolites built up from sodalite units is the double 6-membered ring or hexagonal prism, by which the units are linked. The sodalite unit, or β -cage, can be represented by a truncated octahedron, with the 24 silicon or aluminum atoms (designated T atoms) taking positions at the vertices. The 36 oxygen atoms are displaced from the midpoints of the edges joining the vertices in order to attain tetrahedral configuration around the T atoms. The free diameter of the void within the β -cage is 0.66 nm, but only the smallest molecules can enter through the 0.22 nm diameter opening in the distorted ring of six oxygen atoms associated with each hexagonal face. Each sodalite unit is linked tetrahedrally across hexagonal faces by six bridging oxygens to four other sodalite units. The larger void spaces enclosed by sodalite units and hexagonal prisms are termed α -cages, or supercages. The α -cage is a 26-hedron with a free diameter of ≈ 1.3 nm, and it can be entered through four distorted 12-member rings of diameter 0.80-0.90 nm. In this way each α -cage is tetrahedrally joined to four others giving a complex system of void space extending through the zeolite structure. The α - and β -cages together give Y-zeolites, along with X-zeolites, the largest void volume of any known zeolites, which is ca. 50 v/v % of the dehydrated crystal. From the catalytic viewpoint, the α -cages are by far the most important, since, unlike the β -cages, they permit entry of numerous aliphatic and aromatic compounds.

It has been demonstrated in the present invention these Y-zeolites are particularly effective in the dealumination of aluminosilicate zeolites.

minised form. Preferably, said Y-zeolites are dealuminised by ammonium exchange followed by calcination, or by treatment with ethylenediaminetetraacetic acid (EDTA) or other chelating agents, or by treatment with fluorine or a fluorine-containing compound such as silicon tetrafluoride or ammonium fluorosilicate, or hydrothermal (steam) treatment and/or acid treatment. Said dealuminised Y-zeolites should have a silica-to-alumina molar ratio of greater than three, preferably a ratio of 5 or greater. The examples demonstrate the usefulness of catalysts having a silica-to-alumina ratio of 5 to 100.

Examples of suitable commercially available dealuminised Y-zeolites include UOP's LZY-82 and LZY-72, PQ Corporation's CP-304-37 and CP-316-26, UOP's Y-85, Y-84, LZ-10 and LZ-210.

The unit cell size and $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio for typical dealuminised Y-zeolites are noted in the table below:

	ZEOLITE TYPE	UNIT CELL SIZE, Å	$\text{SiO}_2/\text{Al}_2\text{O}_3$ MOLAR
10	LZY-82	24.53	7.8
15	LZY-85	24.49	9.1
20	LZY-10	24.32	23.7
25	LZY-20	24.35	18.9
30	LZY-84	24.51	8.4
35	LZ-210	24.47	9.9
40	LZY-72	24.52	8.1
45	CP316-26	24.26	45.7

Said catalysts may be in the form of powders, pellets, granules, spheres, shapes and extrudates. The examples described herein demonstrate the advantages of using extrudates.

The reaction may be carried out in either a stirred slurry reactor or in a fixed bed continuous flow reactor. The catalyst concentration should be sufficient to provide the desired catalytic effect.

Etherification to IPTBE can generally be conducted at temperatures from 20° to 250°C; the preferred range is 40° to 80°C. Good results are observed throughout this temperature range. However, it can be noted that the best conversion figures for IPTBE and MTBE cogeneration are observed when the temperature is 20°-100°C. The total operating pressure may be from 0 to 5000 psig (0.1 to 35 MPa), or higher. The preferred pressure range is 100 to 1000 psig (0.7 to 7 MPa).

Typically, IPTBE is generated continuously in up to ca. 15 wt% concentration or greater in the crude liquid product at total liquid hourly space velocities (LHSV) of up to 6 or higher and relatively mild conditions, where:

$$\text{LHSV} = \frac{\text{Volume Of Total Liquid Feed Run Through The Reactor Per Hour}}{\text{Volume of Catalyst In Reactor}}$$

Conversions of isopropanol (IPA) are estimated in the following examples using the equation:

$$\frac{(\text{Mole}\% \text{ of IPA in Feed} - \text{Mole}\% \text{ of IPA in Product})}{\text{Mole}\% \text{ of IPA in Feed}} \times 100$$

The examples which follow illustrate the two-step synthesis of IPTBE and MTBE from acetone, also containing methanol plus *t*-butanol, using cationic resins, β -zeolites, metal-modified β -zeolites and dealuminised Y-zeolites.

The accompanying examples illustrate:

1. The hydrogenation of a crude acetone by-product stream from a MTBE/PO Unit over a bulk metal, nickel-rich, catalyst under moderate conditions (see Example 1).
2. The cogeneration of IPTBE/MTBE from the hydrogenated acetone stream of Example 1 under mild conditions using a β -zeolite catalyst (see Example 2).
3. The cogeneration of IPTBE/MTBE from the hydrogenated acetone stream of Example 1 under mild conditions using a cationic resin catalyst (see Example 3).
4. The generation of IPTBE from an equimolar isopropanol/ *t*-butanol mixture under mild conditions using a β -zeolite or cationic resin catalyst (see Examples 4 and 5).
5. The cogeneration of IPTBE/MTBE from another hydrogenated acetone (73%) stream by passage over a β -zeolite, or cationic resin catalyst (see Examples 6 and 7).
6. The generation of IPTBE from a third hydrogenated acetone (15%) stream by passage over a β -zeolite or cationic resin catalyst (see Examples 8 and 9).

7. IPTBE generation from the hydrogenated acetone stream of Examples 8 and 9, using as the catalyst:
- a) A platinum-impregnated β -zeolite (Example 10).
 - b) A palladium-impregnated, fluorided β -zeolite (Example 11).
 - c) A chromium, manganese, iron-modified (β -zeolite (Example 12).
 - d) A nickel, copper-treated β -zeolite (Example 13).
 - e) A dealuminised Y-zeolite (Example 14).

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EXAMPLE 1

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This example illustrates the hydrogenation of a crude acetone stream.

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A crude acetone mix from a PO/MTBE unit containing 62% acetone (Ac_2O) and having the composition shown in Table 1 was passed, upflow, over a nickel, copper, chromium bulk metal catalyst containing about 72% nickel in the presence of hydrogen (90 l/hr) at LHSV of 0.5 at a series of temperatures (120°-160°C). Hydrogenation of said stream was achieved at 160°C and a typical product composition for the liquid fraction is given in Table 1.

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Estimated acetone conversion is 99%.

The primary product is isopropanol (IPA). Other organic oxygenates identified in this product fraction include methanol (MeOH), *t*-butanol (*t*BA), *t*-butyl formate (*t*BF) and allyl *t*-butyl peroxide (ATBP).

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TABLE I
CRUDE ACETONE HYDROGENATION

Ex.	Catalyst	Temp. (°C)	LHSV	Sample	Composition (%) ^a			tBF	ATBP
					MeOH	Ac ₂ O	tBA		
1	Ni 2715			FS-1	13.9	61.7	0.1	16.7	0.1
		160	0.5	1	15.8	0.8	48.3	30.8	-

^aDesignations: Methanol (MeOH), Acetone (Ac₂O), Isopropanol (IPA), t-Butanol. (tBA), t-butyl Formate (tBF), Allyl t-Butyl Peroxide (ATBP).

EXAMPLE 2

This example illustrates the cogeneration of isopropyl t-butyl ether (IPTBE) and methyl t-butyl ether (MTBE) from a hydrogenated acetone feedstock.

Synthesis was conducted in a tubular reactor (1/2" (12.5 mm) i.d., 12" (300 mm) long) constructed of 316 stainl ss steel, op rated upfl w, and mounted in a furnace, controllable to $\pm 1.0^{\circ}\text{C}$, and fitted with pumps allowing fl w control to $<1\pm$ cc/hr. Th r actor was als fitted with a pressur regulating d vic and equipm nt for monitoring temperature, pressure, and flow rat .

5 The reactor was charged at the beginning of the experiment with 50cc of β -zeolite (80% beta, 20% alumina binder, in 1/16" (1.6 mm) diameter extruded form). A glass wool screen was placed at the top and bottom f the reactor to ensure the catalyst would remain in the middle portion.

The catalyst bed was treated with the crude hydrogenated acetone feedstock of Example 1, while the reactor was held at a series of temperatures ($40^{\circ}\text{-}100^{\circ}\text{C}$). Total unit pressure was maintained at about 700 psi 10 (4.9 MPa). Samples of crude product effluent were collected periodically on stream, in 316ss bombs, and analyzed by glc and gc-ms. Typical analyses data are summarized in Table 2.

At 80°C : The t-butanol conversion level is 41%
(Sample 6).

The MTBE molar selectivity is 76%.

15 The IPTBE molar selectivity is 16%.

Some diisopropyl ether (DIPE), isobutylene, diisobutylene (C_8H_{16}) and water were also generated as co-products of this etherification.

Product identification was by a combination of gc-ms and glc techniques.

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TABLE 2

IPTBE SYNTHESIS

Ex.	Catalyst	Temp.(°C)	Sample	PRODUCT COMPOSITION (Wt%)								II-D			
				DME	C ₄ H ₈	MeOH	Ac ₂ O	IPE	IPA	tBA	MTBE	IPTB			
2	Cr61p ^a		Feed	-	-	15.9	0.8	48.2	30.8	0.1	-	3.0	-	5.6	
		40	1	-	0.1	15.4	0.8	48.1	30.7	0.7	0.1	0.5	2.9	-	5.9
			2	-	0.1	15.3	0.8	47.8	30.8	0.7	0.1	0.6	2.9	-	5.6
		60	3	-	0.5	14.8	0.8	47.8	27.8	2.5	0.1	1.7	2.8	-	6.3
			4	-	0.5	14.9	0.8	47.9	27.6	2.4	0.1	1.7	2.8	0.1	6.4
		80	5	-	1.5	11.7	0.9	48.7	18.4	11.3	-	3.0	2.6	0.1	8.7
			6	-	1.5	11.7	0.9	48.7	18.2	11.4	0.1	3.1	2.6	0.1	8.8
		100	7	0.1	2.6	11.3	0.9	48.9	14.2	13.3	0.1	3.1	2.6	0.8	9.5
			8	0.1	2.6	11.2	0.9	48.9	14.2	13.3	0.1	3.1	2.6	0.8	9.5

^aRun at LHSV 0.5, 700 psig (4.9 MPa)

EXAMPLE 3

This example illustrates the cogeneration of isopropyl *t*-butyl ether (IPTBE) and methyl *t*-butyl ether (MTBE) from a hydrogenated acetone feedstock.

5 Synthesis was conducted using the equipment and procedures of Example 2. The reactor was charged with 50cc of Amberlyst® A-15 (a sulfonated, styrene-divinylbenzene resin in bead form, presoaked in isopropanol) and the catalyst bed was treated with the crude hydrogenated acetone feedstock of Example 1, at a series of temperatures (40°-100°C).

10 Typical analyses results are summarized in Table 3.
At 80°C: The *t*-butanol conversion level is 47%
(Sample 6).
The MTBE molar selectivity is 81%.
The IPTBE molar selectivity is 14%.

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TABLE 3
IPTBE SYNTHESIS

Ex.	Catalyst	Temp. (°C)	Sample	PRODUCT COMPOSITION (W%)								He		
				DME	C ₄ H ₈	MeOH	Ac ₂ O	IPE	IPA	tBA	MTBE	IPTBE		
3	A-15 ^a	Feed	Feed	-	15.7	0.8	48.2	30.9	0.1	-	-	30	-	5.7
	40	1	-	0.7	15.0	0.8	48.2	28.4	2.3	0.1	0.9	2.9	-	6.4
		2	-	0.6	15.1	0.8	48.4	28.0	2.3	0.1	0.9	2.9	-	6.6
	60	3	-	0.9	12.2	0.8	48.8	19.2	10.6	0.1	1.3	2.8	-	8.6
		4	-	0.9	12.1	0.8	48.8	19.4	10.4	0.1	1.2	2.7	-	8.5
	80	5	-	1.3	10.9	0.9	49.2	15.8	14.2	0.1	1.0	2.5	-	9.4
		-6	-	1.3	10.8	0.9	48.8	16.5	13.9	0.1	1.2	2.5	-	9.2
	100	7	0.1	2.2	11.0	0.9	48.1	15.1	13.4	0.4	3.0	2.4	0.1	9.1
		8	0.1	2.2	11.0	0.9	48.3	15.1	13.3	0.4	3.0	2.4	0.1	9.0

^aPresoaked in isopropanol.
^bRun at LHSV 0.5, 700 psig (4.9 MPa)

EXAMPLES 4 AND 5

These examples illustrate the generation of isopropyl t-butyl ether from a mixture of *t*-butanol and isopropanol.

5 Syntheses were conducted using the equipment and procedures of Example 2. The reactor was charged with 50cc of catalyst (either β -zeolite or cationic resin) and the catalyst bed was treated with a 1:1 molar mix of *t*-butanol and isopropanol over a range of temperatures (40°-140°C) and LHSV's (0.25→4).

Typical results are summarized in Tables 4 and 5.

At 60°C, using β -zeolite (C861 β) as catalyst:

10 The *t*-butanol conversion is 25%.

IPTBE effluent concentration is 14.4%.

At 60°C, using cationic resin (A-15) as catalyst:

The *t*-butanol conversion is 24%.

IPTBE effluent concentration is 15.3%.

15 Significant quantities of diisopropyl ether (DIPE) and diisobutylene (C_8H_{16}) were generated at the higher operating temperatures (100°-140°C). Product identification was by gc-ms and glc techniques.

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TABLE 4
IPTBE SYNTHESIS

Ex.	Catalyst	Temp. (°C)	LHSV	Time (Days)	Sample	PRODUCT COMPOSITION (%)					
						C ₁ H ₆	C ₂ H ₆	2-ProH	tBA	DIPE	IPTBE
4	C861β	-	-	-	FS-1	-	-	33.0	66.8	-	-
		100	0.5	1	1	0.1	5.4	30.7	19.4	0.6	3.9
				2	0.1	-	-	-	-	-	-
		120	-	2	3	0.8	2.7	25.0	6.1	5.7	1.1
				4	4	1.0	2.7	24.3	5.4	6.4	0.9
		140	-	3	5	5.5	0.6	10.6	1.5	16.6	0.2
				6	6	5.6	0.6	9.7	0.9	16.9	0.2
		60	-	4	7	-	5.3	28.5	50.4	0.1	14.3
				8	8	5.4	28.2	50.3	0.2	14.4	0.7
		80	-	5	9	-	8.1	28.8	44.5	0.1	12.3
				10	10	7.9	28.7	43.9	0.1	12.2	5.3
		60	0.25	b	11	-	5.4	28.3	50.1	0.1	14.7
				12	12	5.4	28.3	50.3	0.1	14.7	5.5
		80	-	7	13	-	7.4	29.1	43.7	0.1	11.7
				14	14	7.3	29.3	43.8	0.1	11.7	6.6
		40	-	8	15	-	1.5	30.9	60.6	-	6.7
				16	16	1.6	30.8	60.2	0.1	7.0	0.1
											1.5
											1.6

^aNo analyses data.

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TABLE 5
IPTBE SYNTHESIS

Ex.	Catalyst	Temp. (°C)	LHSV	Time (Days)	Sample	PRODUCT COMPOSITION (%)							
						C ₁ H ₆	C ₂ H ₄	2-ProH	tBA	DIPE	IPTBE	C ₆ H ₁₆	H ₂ O
5	A-15 ^a	-	-	-	FS-1	-	-	32.9	66.9	-	-	-	0.1
		40	0.5	1	1	-	3.3	29.3	55.2	0.1	11.7	0.1	2.9
				2	2	-	3.3	29.2	55.3	0.1	11.8	-	2.7
		60	-	-	3	-	4.9	28.3	51.2	0.1	15.1	0.1	3.8
				-4	-4	-	5.2	28.2	50.8	0.1	15.3	0.1	3.8
		80	-	-	5	0.1	8.2	28.2	46.5	0.2	13.6	1.0	4.4
				6	0.1	8.2	28.6	47.4	0.2	13.9	0.8	4.5	
		100	-	-	7	0.9	10.8	28.2	41.8	0.6	10.2	6.0	5.9
					8	0.9	11.0	28.4	41.4	0.6	10.3	6.1	5.9
		60	1.0	-	9	-	5.8	28.5	50.9	0.1	14.4	-	3.7
					10	-	5.9	28.4	50.7	0.1	14.5	0.1	3.7
		60	4.0	-	11	-	6.4	30.5	55.2	0.1	7.2	-	2.7
					12	-	6.4	30.8	55.3	0.1	7.1	-	2.7

^aPresoaked overnight in isopropanol.

EXAMPLES 6 AND 7

The examples illustrate the co-generation of isopropyl t-butyl ether (MTBE) from a hydrogenated acetone feedstock.

5 Syntheses were conducted using the equipment and procedures of Example 2. The reactor was charged with 50cc of catalyst (either β -zeolite or cationic resin) and the catalyst bed was treated with a crude acetone feedstream containing 73% acetone, methyl formate (MeF), methanol (MeOH), t-butanol (tBA), di-t-butyl peroxide (DTBP) plus butanes, that had been hydrogenated by the procedure of Example 1, to convert the acetone fraction to isopropanol (IPA) and then blended with additional t-butanol to a IPA:tBA molar ratio of 1:1. Etherification of this IPA:tBA mix to IPTBE plus MTBE was conducted over a range of operating temperatures. Typical results are summarized in Tables 6 and 7.

10 At 80°C, using the cationic resin (A-15) as catalyst:

15 The t-butanol conversion is 34%.

15 IPTBE molar selectivity is 26%.

15 At 80°C, using the β -zeolite (C861 β) as catalyst:

20 The t-butanol conversion is 44%.

20 IPTBE effluent concentration is 7.3%.

Some isopropyl formate (IPF), isobutylene, diisobutylene (C_8H_{16}) and water were also generated as co-products during these etherification experiments. Product identification was by a combination of gc-ms and glc techniques.

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TABLE 6
IPTBE SYNTHESIS

Ex.	Catalyst	Temp. (°C)	Feed Rate (cc/hr)	PRODUCT COMPOSITION (wt%)											
				MeOH+	Sample	C ₄ H ₈	MeF	IPA	TBA	MTBE	IPF	IPTBE			
6	A-15 ^a		FS-1	-	20.3	26.3 ^c	52.6	-	-	-	-	0.6	0.5	15.1	
		40	12	1	1.8	5.8	26.5	40.5	14.1	3.4	6.9	-	0.8	4.6	2.3
			2	1.8	5.9	26.3	40.8	13.9	3.4	6.8	-	0.8	4.8	2.2	
		60	12	3	2.4	4.0	26.8	35.7	19.0	3.6	7.3	-	0.8	5.9	2.8
			4	2.6	3.9	26.4	35.8	19.2	3.6	7.3	-	0.8	5.8	2.8	
		80	12	-5	4.2	4.1	25.9	34.5	18.4	3.6	7.3	0.4	0.8	5.9	4.1
			6	4.1	4.3	26.5	34.0	18.5	3.6	7.1	0.4	0.8	5.9	4.3	
		100	12	7	6.0	4.4	25.9	31.0	17.3	3.5	6.7	1.9	0.7	6.1	5.8
			8	5.7	6.2	23.5	33.1	16.0	3.3	6.1	2.4	0.7	6.0	5.9	

^aPresoaked in isopropanol.

^bRun at LHSV 0.25, 700 psig (4.9 MPa).

^cIPA:TBA molar ratio 1:1.

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TABLE 7
IPTBE SYNTHESIS

Ex.	Catalyst	Temp. (°C)	Feed Rate (cc/hr)	PRODUCT COMPOSITION (wt%)								MeF ^b	
				MeOH ^a	C ₄ H ₈	MeF	IPA	IBA	MTBE	IPF	IPTBE		
7	C861f			FS-1	1.5 ^c	10.7	29.2 ^b	57.6	-	-	-	0.7	7.7
		40	12	1	2.6	8.8	26.5	49.2	5.0	2.4	4.6	0.7	2.1
				2	1.6	9.2	26.0	49.4	4.8	2.4	4.6	0.7	1.9
		60	12	3	4.2	5.5	25.8	39.1	13.6	3.2	7.4	0.2	0.8
				4	4.2	5.5	25.7	39.1	13.6	3.1	7.5	0.2	0.8
		80	12	-5	6.2	4.2	25.8	32.2	17.5	3.5	7.3	1.8	0.8
				6	5.8	4.1	25.9	32.6	17.3	3.5	7.3	1.8	0.8
		100	12	7	7.5	5.1	25.7	24.8	14.8	3.4	5.1	10.0	0.7
				8	7.4	5.2	25.8	25.0	14.7	3.4	5.1	9.9	0.7
													8.6
													6.5

^aIn-Butane added to feed in the run.

^bIPA:IBA molar ratio 1:1.

EXAMPLES 8 AND 9

These examples illustrate the generation of isopropyl *t*-butyl ether (IPTBE) from a hydrogenated acetone feedstock.

5 Syntheses were conducted using the equipment and procedures of Example 2. The reactor was charged with 50cc of catalyst (either β -zeolite or cationic resin) and the catalyst bed was treated with a crude acetone feedstream containing 15% acetone, methyl formate, methanol, isopropanol, *t*-butanol, di-*t*-butyl peroxides plus butanes, that had been hydrogenated by the procedure of Example 1 to convert said acetone fraction to additional isopropanol. The IPA:fBA molar ratio of the final feed mix was 1:3.8. Etherification to IPTBE was 10 conducted over a range of temperatures (40°-100°C). Typical results are summarized in Tables 8 and 9.

At 60°C, using the cationic resin (A-15) as catalyst:

The *t*-butanol conversion is 12%.

IPTBE molar selectivity is 42%.

At 60°C, using the β -zeolite (C861 β) as catalyst:

15 The *t*-butanol conversion is 12%.

IPTBE effluent concentration is 6.5%.

Typical IPTBE product was then isolated by fractional distillation of the crude effluent material of Example

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TABLE 8
IPTBE SYNTHESIS
PRODUCT COMPOSITION (w%)

Ex.	Catalyst	Temp. (°C)	Feed Rate (cc/hr)	PRODUCT COMPOSITION (w%)										
				MeOH+ Sample	C ₄ H ₈	MeF	IPA	tBA	MTBE	IPF	IPTBE	C ₆ H ₁₆	DTBP	
8	A-15 ^a	-	-	FS.1	0.9 ^c	3.5	11.2 ^d	81.4	-	-	-	2.8	0.1	3.1
		40	12	1	5.0	0.8	9.6	74.4	1.0	6.0	0.1	2.9	3.8	4.6
			2	4.8	0.8	9.7	74.5	1.0	5.9	0.1	2.8	3.9	4.4	
		60	-3	7.3	0.7	9.4	71.5	-	1.0	6.5	0.3	2.9	5.0	7.4
			4	7.4	0.6	9.2	71.9	-	1.0	6.5	0.2	2.9	4.8	7.4
		80	5	10.7	0.7	9.4	67.4	-	0.9	5.8	1.6	2.9	6.3	10.8
			6	10.8	0.7	9.4	61.9	5.4	1.0	5.8	1.6	2.8	6.2	11.1
		100	7	13.7	0.9	9.2	53.5	6.0	0.9	4.4	6.9	2.8	7.7	13.5
			8	13.9	0.9	9.2	53.5	6.0	0.9	4.4	6.9	2.8	7.6	14.1

^aPresoaked in isopropanol.^bRun at LHSV 0.25, 700 psig (4.9 MPa)^cFeed contains n-butane.^dIPA:tBA molar ratio 1:3.8.

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TABLE 9

IPTBE SYNTHESIS

Ex.	Catalyst	Temp. (°C)	Feed Rate (cc/hr)	PRODUCT COMPOSITION (wt%)											
				MeOH+	Sample	C ₂ H ₆	MeF	IPA	tBA	MTBE	IPF	IPTBE	C ₄ H ₁₀	DTBP	H ₂ O
9	C861/F	-	FS-1	0.9 ^a	3.4	11.3 ^c	-	81.2	0.1	0.1	-	-	2.8	0.2	3.2
		40	12	1	3.8	2.4	9.7	75.9	-	0.5	4.4	0.2	2.8	2.5	4.2
			2	3.8	2.3	9.6	76.0	-	0.5	4.5	0.1	2.8	2.5	4.2	
		60	-3	7.3	0.9	9.1	71.5	-	0.7	6.5	0.8	2.9	4.7	6.8	
			4	7.2	1.0	9.1	71.5	-	0.8	6.5	0.7	2.9	4.6	7.4	
		80	5	9.9	0.8	9.3	65.3	-	0.8	5.5	4.0	2.9	6.5	9.9	
			6	9.5	0.7	9.3	60.9	5.0	0.8	5.5	4.0	3.0	6.5	9.0	
		100	7	10.0	1.1	9.6	45.8	5.8	0.7	3.5	16.4	2.9	10.6	10.3	
			8	9.8	1.0	9.8	47.1	5.8	0.8	3.6	15.8	2.9	10.2	10.4	

^aRun at LHSV 0.25, 700 psig (4.9 MPa).^bFeed contains n-butane.^cIPA:tBA molar ratio 1:3.8.

EXAMPLE A

This example illustrates the preparation of platinum-treated β -zeolite.

- 5 To a sample of β -zeolite (50% beta, 50% alumina, 1/16" (1.6 mm) diameter extruded form, 300cc, 176g) was added a solution of tetraamine platinum(II) nitrate ($\text{Pt}(\text{NH}_3)_4(\text{NO}_2)_2$, 1.75g) in 120cc of distilled water, with stirring. After mixing for up to 1 hour, the solid was dried at 120°C for 2 hours, calcined at 540°C for 3 hours, and reduced in a stream of hydrogen at 400°C for 4 hours.

EXAMPLE B

- 10 This example illustrates the preparation of a nickel, copper treated β -zeolite.

- To a sample of β -zeolite (80% beta, 20% alumina, 1/16" (1.6 mm) diameter extruded form, 100g) was added a solution of nickel nitrate (5.05g) plus copper nitrate (3.74g) in distilled water (88cc), with stirring after mixing for up to 1 hour, the solid was dried at 120°C for 2 hours, calcined at 315°–480°C for 12 hours, and reduced in a stream of hydrogen at 350°C for 4 hours.

EXAMPLE C

This example illustrates the preparation of a chromium, manganese, iron-treated β -zeolite.

- 20 To a sample of β -zeolite (80% beta, 20% alumina, 1/16" (1.6 mm) diameter extruded form, 92g) was added a solution of ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 4.57g), chromium(III) nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 7.27g) and manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4.93g) dissolved in 90cc of distilled water, with stirring. After mixing for up to 1 hour, the solid was dried at 120°C, overnight, calcined at 315°–540°C for 4 hours, and reduced in a stream of hydrogen at 350°C.

25 **EXAMPLES 10-14**

These examples illustrate the generation of isopropyl t-butyl ether (IPTBE) from a hydrogenated acetone feedstock.

- 30 Syntheses were conducted using the equipment and procedures of Example 2 and the hydrogenated acetone feedstock of Examples 8 and 9. The metal-modified β -zeolite catalysts demonstrated to be effective for IPTBE/MTBE cosynthesis include:

- a) The platinum-impregnated β -zeolite of Example A (See Table 10).
b) A palladium-impregnated, fluorided β -zeolite (See Table 10).
c) The chromium, manganese, iron-modified β -zeolite of Example C (See Table II).
d) The nickel, copper-treated β -zeolite of Example D (See Table II).

Isopropyl t-butyl ether generation was also realised with a dealuminised Y-zeolite, CP316-26 from PQ Corp. (See Table 12).

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TABLE 10

IPTBE SYNTHESIS

Ex.	Catalyst	Temp. (°C)	Feed Rate (cc/hr)	Sample	PRODUCT COMPOSITION (wt%)							
					C ₄ H ₈	MeOH + MeF	IPA	tBA	MTBE	IPF	IPTBE	C ₆ H ₁₀
10	Ex. A*	7055-49R-2	FS-1	0.9	3.4	11.3	81.2	0.1	0.1	-	-	2.8
				1	6.3	1.5	9.3	73.0	0.6	5.9	0.3	2.9
		60	12	2	6.6	1.3	9.3	68.3	4.2	0.6	6.0	0.5
												4.1
	80		3	10.6	0.8	9.4	60.2	6.1	0.7	5.5	3.1	2.9
				4	10.0	0.8	9.5	61.1	5.9	0.7	5.5	2.9
11	Pd/F/ ¹⁸ F		FS-1	0.5	2.1	11.3	82.2	-	0.2	-	-	2.8
		60	12	1	6.7	1.2	9.3	67.7	4.3	0.6	6.1	0.6
				2	6.6	0.9	9.4	67.8	4.7	0.6	6.0	0.5
	80		3	10.5	0.6	9.4	59.6	6.3	0.7	5.4	3.5	2.8
				4	9.7	0.7	9.5	60.6	6.2	0.7	5.4	3.0
												9.4
												9.6

*0.3% Pt on 50% beta/alumina, recovered at 400°C.
**0.3% Pd, 1%F, on 50% beta/alumina, recovered at 200°C.

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TABLE 11

IPTBE SYNTHESIS

Ex.	Catalyst	Temp. (°C)	Feed Rate (cc/hr)	Sample	PRODUCT COMPOSITION (w%)									
					C ₄ H ₈	MeOH + MeF	IPA	1BA	MTBE	IPF	IPTBE	C ₆ H ₁₆	DTBP	H ₂ O
12	Ex. C ^a		FS-1	0.9	3.4	11.3	81.2	0.1	0.1	-	-	2.8	0.2	
				60	12	1	6.9	1.0	9.3	68.1	4.4	0.6	5.9	0.4
60			FS-1	2	6.6	1.0	9.3	68.5	4.3	0.6	5.9	0.4	2.8	4.6
				60		3	10.7	0.7	9.4	60.8	6.2	0.7	5.6	2.2
13	Ex. B ^b		FS-1	4	10.6	0.7	9.4	60.8	6.2	0.7	5.6	2.2	2.9	6.3
				60		4	10.7	0.7	9.4	61.2	0.1	0.1	-	2.8
80			FS-1	1	5.1	1.6	9.8	75.5	-	0.4	4.4	0.1	2.0	3.1
				2	5.0	1.5	9.8	75.5		0.4	4.4	0.1	2.1	2.9
80			FS-1	3	10.9	0.8	9.4	62.5	5.8	0.6	5.7	1.2	1.9	5.9
				4										

^a1% Cr, 1% Mn, 1% Fe on 80% beta, 20% alumina.^b1% Ni, 1% Cr on 80% beta, 20% alumina, reduced at 350°C.

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TABLE 12

(PTBE SYNTHESIS

Ex.	Catalyst	Temp. (°C)	Feed Rate (cc/hr)	Sample	PRODUCT COMPOSITION (wt%)							
					C ₄ H ₈	MeOH+	MeF	IPA	¹ BA	MTBE	IPF	IPTBE
14	CP316-26*			FS-1	0.5	2.1	11.3	82.5	-	-	-	-
		60	12	1	2.4	2.4	10.0	78.7	-	1.1	2.0	-
				2	2.5	2.4	10.0	78.5	-	1.2	2.2	-
		80		3	8.7	1.1	9.5	66.9	4.7	1.0	4.8	-
				4	7.9	1.1	9.6	67.7	4.5	1.0	4.8	0.1
											2.8	1.8
												4.7

*Y-Zeolite, 1.6mm Extrudates

Claims

1. A two-step process for the generation of isopropyl *t*-butyl ether from a crude by-product acetone stream characterised in that it comprises the steps of:
 - 5 a) Hydrogenating said crude acetone over a bulk metal, nickel-rich catalyst to give an isopropanol-rich effluent;
 - b) subjecting said isopropanol-rich intermediate to etherification conditions in the presence of a strong acid catalyst selected from:
 - (1) a cationic resin;
 - (2) a β -zeolite;
 - (3) dealuminised Y-zeolites; and
 - (4) metal-modified β -zeolites.
2. A process as claimed in Claim 1 wherein the nickel-rich catalyst comprises 60%-85% nickel, 1%-30% copper and 0.1%-6% chromium.
- 15 3. A process as claimed in Claim 1 wherein the etherification catalyst is a cationic resin selected from the group consisting of a gel type resin and a macroreticular ion exchange resin.
4. A process as claimed in claim 1 or claim 2 wherein the etherification catalyst is a β -Zeolite having a silica:alumina molar ratio of at least 10:1.
- 20 5. A process as claimed in any one of claims 1, 2 or 4 wherein the β -zeolite has a surface area, after calcination, of at least 100 m^2/g .
6. A process as claimed in any one of claims 1, 2, 4 or 5 wherein the β -zeolite is modified with one or more metals from Groups IB, VIB, VIIIB and VIII of the Periodic Table.
- 25 7. A process as claimed in claim 6 wherein the β -zeolite is modified with one or more metals selected from the group consisting of iron, chromium, manganese, copper and nickel.
8. A process as claimed in claim 6 wherein the β -zeolite is modified with platinum or palladium.
- 30 9. A process as claimed in any one of claims 6 to 8 wherein the concentrations of metals deposited on said zeolite vary from 0.01% to 10.0% for each metal.
10. A process as claimed in any one of claims 1, 2, and 4 to 9 wherein the β -zeolite catalyst is formed in the presence of a binder selected from a Group III oxide or a Group IV oxide.
- 35 11. A process as claimed in claim 1 or claim 2 wherein the second stage catalyst is a Y-zeolite dealuminised in a manner selected from:
 - a) ammonium exchanging the Y-zeolite followed by calcining;
 - b) treating the zeolite with ethylenediaminetetraacetic acid;
 - c) treating the Y-zeolite with a fluorine-containing compound from the group consisting of silicon tetrafluoride and ammonium fluorosilicate; and
 - d) treating the Y-zeolite with steam alone or followed by acid treatment.
- 40 12. A two-step process for the cogeneration of isopropyl *t*-butyl ether and methyl *t*-butyl ether from a crude by-product acetone stream in accordance with any preceding claim wherein said acetone stream contains 5% or more of both methanol and *t*-butanol.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 9912

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 379 323 (MITSUI PETROCHEMICAL INDUSTRIES, LTD) * page 3 *	1	C07C41/09 C07C29/145 C07C43/04
A	EP-A-0 333 078 (TEXACO DEVELOPMENT CORPORATION) * claims 1,4 *	1,11	
A	US-A-5 214 217 (J.F. KNIFTON) * claim 1 *	1	
P,A	EP-A-0 595 567 (TEXACO CHEMICAL COMPANY) * claims 1,7 *	5,7	
A	CHEMICAL ABSTRACTS, vol. 107, no. 5, 1987, Columbus, Ohio, US; abstract no. 39115u, * abstract * & J. MOL. CATAL., vol.37, no.2-3, 1986 pages 287 - 296 M CASTIGLIONI ET AL	1	

The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
BERLIN	16 March 1995	Kapteyn, H	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			